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Theoretical Study of Doping Limits of CdTe

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ABSTRACT

First-principles total energy and band structure calculations are performed to understand the factors that limit doping in CdTe. We calculated systematically the formation energies and transition energy levels of intrinsic and extrinsic defects. We find that n -type doping in CdTe is limited by the spontaneous formation of the intrinsic closed-shell cation vacancy V_{Cd}^{2-} and DX centers, whereas p -type doping is limited by not having a dopant with both high solubility and shallow acceptor level.

1. Introduction

CdTe is an important material for solar cell applications [1]. However, the dopability in CdTe is relatively low, especially for the p -type doping. This has become one of the main issues in device fabrication using CdTe. The mechanism of the low dopability in CdTe is not well understood. Generally speaking, there are three main factors that could limit the dopability: (i) The dopant may have a low solubility. (ii) The transition energy level may be too high. (iii) The formation of opposite-charged defect or defect complexes. To identify which one of these factors affects the p - or n -type doping in CdTe, we have systematically calculated the formation energies and transition energy levels of intrinsic and extrinsic defects in CdTe using the first-principles band structure method. Our results are discussed below. The general understanding from this study can be used as a guideline of overcoming the doping limit in CdTe.

2. Method of Calculations

The band structure and total energy calculations are performed using the linearized augmented plane wave (LAPW) method within the local density approximation (LDA) [2]. For the defect calculation, we model the system by putting a defect at the center of a 32-atom periodic supercell. To calculate the defect formation energy and defect transition energy levels, we compute the total energy $E(\alpha, q)$ for a supercell containing the relaxed defect α in charge state q and the total energy $E(CdTe)$ in the absence of the defect. From these quantities, we deduce the defect formation energy $\Delta H_f(\alpha, q)$ as a function of the electron Fermi energy ϵ_F and the atomic chemical potentials μ_i [2]. Here, μ_i is set to zero for elements at stable phase and ϵ_F is referenced to the valence band maximum (VBM). Under equilibrium growth condition, $\mu_{Cd} + \mu_{Te} = \Delta H_f(CdTe)$, where $\Delta H_f(CdTe) = -0.79$ eV is the formation energy of CdTe. $\mu_{Cd}=0$ corresponds to the Cd-rich limit, and $\mu_{Te}=0$ corresponds to the Te-rich limit. The defect transition energy level $\epsilon_{\alpha}(q/q')$ is the Fermi energy ϵ_F at which the formation energy $\Delta H_f(\alpha, q)$ of defect α of charge q is equal to that of another charge q' of the same defect.

3. Results

(i) *Formation energy of the neutral point defects:* Table I lists the calculated defect formation energy of point defects at neutral charge state ($q=0$) and $\mu_i=0$. The actual defect formation energy depends on the available chemical potential of the dopants and the chemical potential of host elements. For example, for neutral V_{Cd}^0 , the lowest formation energy occurs at the Cd-poor limit with $\Delta H(V_{Cd}^0)=2.67-0.79=1.88$ eV. For extrinsic defects, μ_A is bounded by the values that lead to the formation of secondary phases such as Na_2Te and $CdCl_2$. For example, for Na_{Cd}^0 , because the calculated formation energy $\Delta H(Na_2Te)=-2.84$ eV, the lowest formation energy occurs at the Cd-poor limit with $\Delta H(Na_{Cd}^0)=0.45-0.79+1.42=1.08$ eV. This is because at the Cd-poor limit, the highest possible μ_{Na} is -1.42 eV. Similarly, because the formation energy of Cu_2Te is close to zero, the lowest formation energy of Cu_{Cd}^0 at the Cd-poor condition is $\Delta H(Cu_{Cd}^0)=1.31-0.79=0.52$ eV. Thus, the solubility of Cu is larger than that of Na. Our analysis indicates that the impurity that does not form strong bonds with the host elements has higher solubility than the impurity which forms strong bonds with the host. It also suggests that using metastable compound (e.g., CuTe) as a dopant can raise the chemical potential of the impurity, and thus, increase the solubility.

(ii) *Defect transition energy levels:* Fig. 1 presents our calculated acceptor transition energy levels, and Fig. 2 gives the donor transition energy levels. Using these values, one can derive the formation energies of charged defects as a function of Fermi energy and chemical potential. For example, Fig. 1 shows that at $\epsilon_F=0.13$ eV above VBM, $E(V_{Cd}^-)$ equals $E(V_{Cd}^0)$, which equals 2.67 eV at the Cd rich limit (Table I). Thus, at VBM where $\epsilon_F=0$, the formation energy of $E(V_{Cd}^-)$ will equal 2.80 eV.

Table I. Calculated formation energies ΔH (in eV) of point defects at neutral charge state ($q=0$) and $\mu_i=0$.

Defect	ΔH	Defect	ΔH
V_{Cd}	2.67	Cd_{Te}	3.92
V_{Te}	3.24	Te_{Cd}	3.70
Te_i	3.41	Cd_i^a	2.26
O_{Cd}	-0.41	Cd_i^c	2.04
Na_{Cd}	0.45	Al_{Cd}	1.17
Cu_{Cd}	1.31	Ga_{Cd}	1.23
Ag_{Cd}	1.32	In_{Cd}	1.23
Au_{Cd}	1.30	F_{Te}	-0.08
N_{Te}	2.62	Cl_{Te}	1.23
P_{Te}	1.83	Na_i^a	0.60
As_{Te}	1.68	Na_i^c	0.45
Sb_{Te}	1.72	Cu_i^a	2.14
Bi_{Te}	1.96	Cu_i^c	2.24

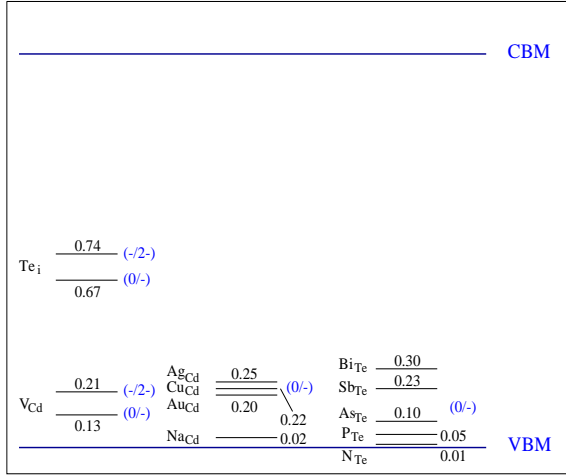


Fig. 1. Calculated acceptor transition energy levels.

Acceptor levels: Fig. 1 shows that for intrinsic defects V_{Cd} has relatively shallow transition energy levels (0/-) and (-2/-) at 0.13 and 0.21 eV above the VBM, respectively. Thus, V_{Cd} is the most important intrinsic acceptor for CdTe. However, the transition energy levels are still too high to reach high hole density. For impurity doping, we find that for A_{Cd} , where $A=Cu, Ag,$ and Au , the calculated (0/-) transition energy levels are at 0.22, 0.25, and 0.20, eV above the VBM, respectively. These (0/-) transition energy levels are relatively deep because of the coupling between the delocalized d orbital of the group IB atom and the Te p orbital. The (0/-) level of Na_{Cd} is much shallower at 0.02 eV above VBM because Na has no active d orbital. Thus, Na_{Cd} could be an important acceptor in CdTe. For B_{Te} impurity doping, where $B= N, P, As, Sb, Bi$, the calculated (0/-) transition energy levels are at 0.01, 0.05, 0.10, 0.23, and 0.30 eV, respectively. The transition energy levels decrease monotonically when the atomic number of B decreases. The shallow (0/-) transition energy levels for N_{Te} and P_{Te} indicate that they could be important p-type dopant for CdTe. Unfortunately, the defect formation energy of N_{Te} and P_{Te} are large (Table I) due to the large size mismatch between the dopants and Te. Thus, the equilibrium solubilities of N and P in CdTe are low. If, however, one can enhance the incorporation of N and P in CdTe through non-equilibrium process (e.g., ion implantation, gaseous source, and electron beam annealing), it may be possible to greatly enhance the hole carrier density in CdTe.

Donor levels: Fig. 2 shows that most intrinsic donor levels are deep inside the band gap. Only Cd_{Te} has a relatively shallow (2+/0) transition energy level at 0.10 eV below the CBM. For impurity doping, we find that for A_{Cd} , where $A=Al, Ga,$ and In , the calculated (+/0) transition energy levels are at 0.02, 0.24, and 0.04 eV below the CBM, respectively. Because Al_{Cd} and In_{Cd} both have very shallow transition energy levels, they could be important n-type dopants in CdTe. For B_{Te} impurity doping with $B=F$ and Cl , we find the calculated (+/0) transition energy levels are very deep inside the band gap due to the large electronegativity of the dopants. The calculated donor (+/0) transition energy

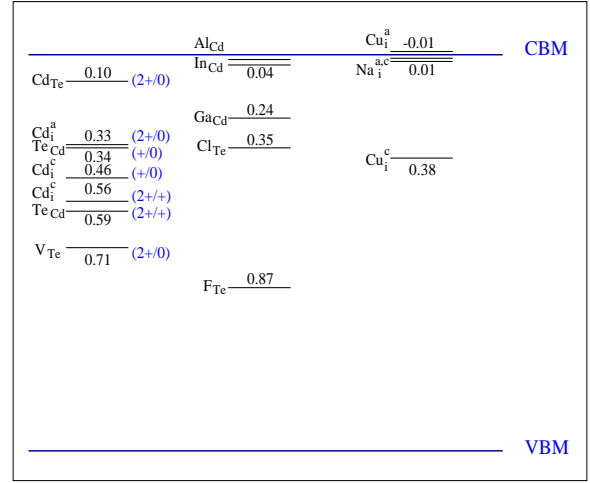


Fig. 2. Calculated donor transition energy levels.

levels are -0.01, 0.01, 0.01, and 0.38 eV, respectively, for Cu_i^a , Na_i^a , Na_i^c , and Cu_i^c . Because Na_i has very shallow donor levels, it could be a strong candidate as an efficient n-type dopant for CdTe.

(iii) **Doping limit:** By plotting defect formation energy as a function of electron Fermi energy, we find that at the Cd-rich limit, undoped CdTe tends to be neutral or slightly n-type. This is because the Fermi energy is pinned near the mid gap by the compensating donor defect Cd_i^{2+} and the acceptor defect V_{Cd}^{2-} . On the other hand, at the Te-rich limit, undoped CdTe tends to be slightly p-type, since the Fermi energy is pinned at a level closer to the VBM. For impurity doping, we find that relatively high n-type doping can be achieved at the Cd-rich limit; but eventually, the n-type doping in CdTe will be stopped by the spontaneous formation of the intrinsic closed-shell cation vacancy V_{Cd}^{2-} when the Fermi energy approaches the conduction band minimum (CBM). For some extrinsic dopant such as In_{Cd} and Al_{Cd} , we find that n-type doping could also be limited by the spontaneous formation of the DX center [3]. For p-type doping, we find that it is not limited by compensating defects. Instead, it is limited by not having a dopant with both high solubility and shallow acceptor level. Some of the dopants have shallow acceptor levels, but their defect formation energies are too high (e.g., CdTe:N or CdTe:P). Other dopants have relatively low formation energy, but their acceptor level is too deep (e.g., CdTe:Cu). In some cases, it is also limited by the formation of compensating interstitial defects (e.g., Na_i in CdTe:Na). We find that the AX center is unstable in CdTe [3].

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